



© The Author 2005. Published by Oxford University Press on behalf of the New York Academy of Medicine. All rights reserved. For permissions, please e-mail: journals.permissions@oupjournals.org
Advance Access publication February 28, 2005

Steel Dust in the New York City Subway System as a Source of Manganese, Chromium, and Iron Exposures for Transit Workers

Steven N. Chillrud, David Grass, James M. Ross, Drissa Coulibaly, Vesna Slavkovich, David Epstein, Sonja N. Sax, Dee Pederson, David Johnson, John D. Spengler, Patrick L. Kinney, H. James Simpson, and Paul Brandt-Rauf

ABSTRACT The United States Clean Air Act Amendments of 1990 reflected increasing concern about potential effects of low-level airborne metal exposure on a wide array of illnesses. Here we summarize results demonstrating that the New York City (NYC) subway system provides an important microenvironment for metal exposures for NYC commuters and subway workers and also describe an ongoing pilot study of NYC transit workers' exposure to steel dust. Results from the TEACH (Toxic Exposure Assessment, a Columbia and Harvard) study in 1999 of 41 high-school students strongly suggest that elevated levels of iron, manganese, and chromium in personal air samples were due to exposure to steel dust in the NYC subway. Airborne concentrations of these three metals associated with fine particulate matter were observed to be more than 100 times greater in the subway environment than in home indoor or outdoor settings in NYC. While there are currently no known health effects at the airborne levels observed in the subway system, the primary aim of the ongoing pilot study is to ascertain whether the levels of these metals in the subway air affect concentrations of these metals or related metabolites in the blood or urine of exposed transit workers, who due to their job activities could plausibly have appreciably higher exposures than typical commuters. The study design involves recruitment of 40 transit workers representing a large range in expected exposures to steel dust, the collection of personal air samples of fine particulate matter, and the collection of blood and urine samples from each monitored transit worker.

KEYWORDS Bioavailability, Chromium, Dose-response, Hazardous air pollutants, Iron, Manganese, Metro, Steel dust, Subway, transit workers, Underground railway.

INTRODUCTION

In this article, we elaborate some of the NYC results reported by Chillrud et al.¹ and describe an ongoing pilot study that is focused on investigating dose–response relationships of steel dust elements in transit workers. Transit workers, because of their work-related activities in the subway system, are likely to have appreciably higher

Dr. Chillrud, Mr. Grass, Mr. Ross, Mr. Epstein, Ms. Pederson, Mr. Johnson, and Dr. Simpson are with the Lamont-Doherty Earth Observatory of Columbia University, Palisades, New York; Dr. Coulibaly, Ms. Slavkovich, Dr. Kinney, and Dr. Brandt-Rauf are with the Joseph A. Mailman School of Public Health at Columbia University, New York, New York; Dr. Sax and Dr. Spengler are with the Harvard School of Public Health, Boston, Massachusetts.

Correspondence: Steven N. Chillrud, Lamont-Doherty Earth Observatory of Columbia University, 61 Rt 9W, Palisades, NY 10964. (E-mail: chilli@ldeo.columbia.edu)

airborne exposures to these metals than the commuting public. Steel dust exposure in the NYC subway system has been of concern to subway workers and transit police for decades.² As one of the largest subway systems in the world, the NYC subway environment could provide important information relevant to evaluating the potential for health effects from exposures to airborne metals.

As recognized by the United States Clean Air Act Amendments of 1990, there is increasing concern about potential effects of low-level airborne metal exposure on cancer,^{3,4} neurodegenerative,^{5,6} respiratory, and cardiovascular diseases.^{7,8} Steel dust can provide an important pathway of airborne exposures for iron (Fe), manganese (Mn), chromium (Cr), and several other metals, depending on the type of steel. Results reported by Chillrud et al.¹ strongly suggest that steel dust exposures obtained while commuting via the NYC subway system substantially increased airborne exposure levels of Fe, Mn, and Cr among high-school students in NYC.

Relatively, few studies have been published on air pollutants found in underground subway systems, but they consistently show elevated particle levels. Levels of fine particulate matter less than 2.5 µm in mean diameter (PM_{2.5}) in the London and Stockholm subway systems have been reported to be very elevated (in the hundreds of micrograms per meter cube). Pollutante Elevated Fe has also been reported for a small number of air samples from subway systems in London, Stockholm, Washington, DC, and Tokyo. Pollutante Fernand Malevels for a study population of over 800 subjects in Toronto and was also found to be important for Mn exposures of London subway riders. Reports available on the web for the London Underground (http://tube.tfl.gov.uk/content/about/report/dust_reports.asp) refer to various data sets collected over 20 years on London Underground Dust.

Potential Health Effects

Iron exposure together with other transition metals has been speculated to influence a host of negative health outcomes related to its ability to generate free radicals in the body.^{7,17} Disorders in Fe metabolism, either systemically or locally in the brain, have been linked to a number of neurodegenerative diseases such as Parkinsonism, Alzheimer's disease, and multiple sclerosis.¹⁷ Excess accumulation of Fe has been seen in basal ganglia, an area of the brain that controls body movement, in Parkinson's patients. It has been suggested that defects in Fe metabolism or altered Fe homeostasis may contribute, at least partly, to the etiology of Parkinsonism.¹⁷ However, no epidemiological evidence of which we are aware has indicated that exposure to relatively low air levels of Fe would lead to Parkinsonism. Welders have been shown to be at greater risk for pneumonia, possibly because Fe can act as a growth factor for bacteria.

The relationship between Mn intoxication and Parkinsonism has long been recognized.¹⁹⁻²² Health risks of exposure to Mn have been associated with organic Mn-containing pesticides, such as manganese ethylene-bis-dithiocarbamate and inorganic Mn dust or vapor among steel manufacturing workers or welders.¹⁹ The latter occupation appears to be one of the more common sources of exposure in work settings.

Chromium is a metal known for its carcinogenesis. Past studies have shown that exposure to Cr, particularly in chrome production and chrome pigment industries, is associated with cancer of the respiratory tract.²³ Chromium in the body can form coordination covalent interactions with DNA, and this can subsequently lead to gene mutation, DNA lesions, and arrest of DNA replication. It has

been shown that detection of DNA-protein complexes may serve as a useful biomarker of exposure for monitoring Cr exposure.²⁴ Excess cancer risks can be estimated from average lifetime exposure levels to Cr. ^{25,26} On the basis of the total Cr levels observed for commuting students, life-long commuters have an estimated excess cancer risk of roughly 1 in 100,000. Subway workers can be expected to have appreciably higher exposures than the commuting public to steel dust, and thus higher estimated risks of excess cancer. Although excess cancer-risk estimates may be indicative of potential hazards faced by transit workers, there are many uncertainties associated with methods for estimating cancer risk, including that the oxidation state of Cr is important to its toxicity, with Cr(VI) being considerably much more toxic than Cr(III). Most exposure studies including this one report total Cr concentrations, not segregated by oxidation state. Steel dust generated in subway environments could include a significant amount of Cr(VI), based on results of a study of fumes generated during welding of steel where most of the airborne Cr was Cr(VI).²⁷ Compared with total Cr, estimated excess cancer risk from Cr(VI) may be as much as 10 times higher for an equivalent exposure level.26,28

Prior Results on High-School Students' Personal Air Samples

The study design and methods of an earlier NYC subway study we conducted are described in more detail elsewhere. High-school students from NYC were monitored for fine particulate matter in both winter 1999 (n=38) and summer 1999 (n=41). Sampling was carried out simultaneously over 48-hour periods at several locations: (1) inside the home, (2) outside the home, (3) on the person, and (4) at two fixed sites (urban and upwind of NYC). More than half of the students reported riding the subway for some portion of the 48-hour monitoring periods.

Cumulative frequency distributions of metal concentrations by sampling environment revealed that several metals had significantly higher concentrations for personal samples than for the other sample types. This enrichment was particularly large for several elements including Fe, Mn and, Cr (Fig. 1A, B, and C).

Particulate concentrations of Fe and Mn (mass of metal per mass of PM_{2.5}) were strongly correlated for each type of sample. The least squares regression slope of particulate Fe on particulate Mn concentrations (R^2 =0.98) for personal samples was 104, approximately twice the ratio of 55 that is representative of average crustal material (i.e., typical dirt),³⁰ suggesting a noncrustal source. Home indoor and ambient outdoor air samples had Fe/Mn slopes similar to crustal material (Fig. 2A and B). For particulate concentrations of Cr and Mn, the slope of the personal samples (0.33) was three times the crustal ratio of Cr to Mn.¹ In October 2001, two personal samplers and a particle counter were carried into the NYC subway system for approximately 8 hours to collect a single set of duplicate PM_{2.5} samples that integrated roughly 5 hours in underground subway stations and about 3 hours in subway cars. The average ratio of Fe to Mn and Cr to Mn for the duplicate subway samples was 107 and 0.34, respectively, consistent with subway air being the predominant source of Fe, Mn, and Cr in the elevated personal samples of urban students (Fig. 2A).

Particle-counter data on several aerodynamic size ranges > $0.3 \,\mu m$ indicated that particle numbers within air conditioned subway cars were roughly 10% to 25% of levels in subway stations depending on the aerodynamic size

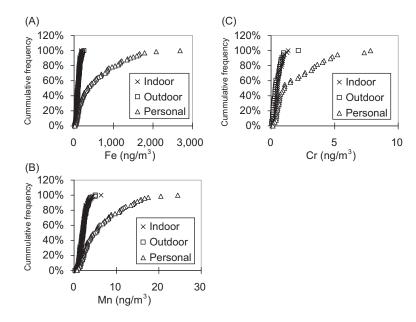


FIGURE 1. Cumulative frequency distributions for (A) iron (Fe), (B) manganese (Mn), and (C) chromium (Cr) concentrations in air. Personal air samples were elevated in comparison to indoor and outdoor samples.

range being counted, suggesting that filtration provided by subway air conditioners is very effective in reducing particulate concentrations within the subway cars.

Iron, manganese, and chromium which were the most enriched in subway air compared with outdoor air samples (Fig. 3), are present in significant concentrations in many types of steel. Steel dust may be rendered airborne by friction erosion of subway rails, wheels and brushes as hypothesized by others. ^{15,16} The airborne

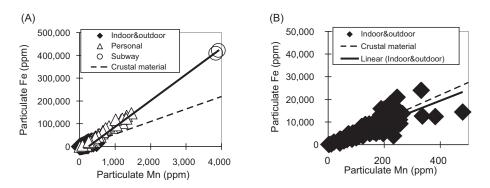


FIGURE 2. (A) The ratios of particulate iron (Fe) to manganese (Mn) observed in personal air samples were similar to the Fe/Mn ratio measured in a single set of duplicate samples collected in the subway system (solid line drawn by hand). Home indoor and outdoor location Fe/Mn ratios were similar to average crustal values³⁰ represented by the dashed line. (B) Expansion of the home indoor and outdoor sample data is shown separately (note different scales) where a least squares fit line to the data has a slope of 48.

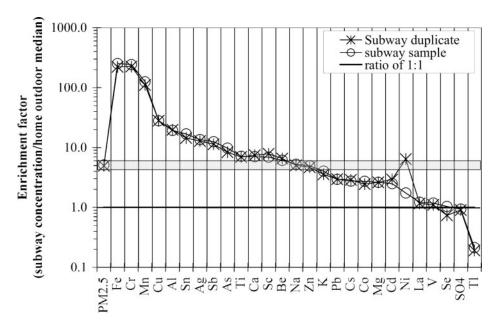


FIGURE 3. Enrichment of subway samples as defined by the ratio of air concentration in an 8-hour sample from the NYC subway to the median air concentration measured on the set of 41 home outdoor locations throughout NYC collected in the summer of 1999 in the Toxic Exposure Assessment, a Columbia and Harvard (TEACH) study. The transparent box is placed to show which elements are elevated above and below the enrichment factor for $PM_{2.5}$.

subway levels of these three metals were more than 100 times greater than levels observed in home indoor or outdoor settings in NYC.¹ Nickel was not elevated in the subway samples relative to the enrichment factor for PM_{2.5} (Fig. 3), which together with the Fe, Mn, and Cr data indicates that the steel used in the NYC subway system is similar to steel type "AISI-SAE 5046H."³¹ Additional elements measured in the subway duplicate samples that were enriched above median outdoor air levels by an order of magnitude or more include Al, Cu, Sn, Ag, Sb, and As; potential subway sources of many of these elements include contact points for electrical relays and switches, composite-metal break pads, and trace contaminant levels in some types of steels.

Figure 4 shows that students who did not ride the subway had personal exposures of Mn very similar to the levels measured in ambient and home indoor environments, whereas the students who rode the subway had levels of Mn that were significantly elevated above levels in ambient and home indoor settings. The same trend was observed for Fe¹ and Cr.

All of the data above suggest that the subway system represents an important source for chronic exposures to airborne metals. From the point of view of the commuting public, the total population exposed is large (millions per day), and the total length of exposure could represent decades of daily commuting. However, many transit workers in the subway could have appreciably higher exposures to steel dust than commuters because of greater time within the subway system as well as explicit work-related activities. For example, maintenance and repair activities can potentially increase workers' exposure to steel dust.

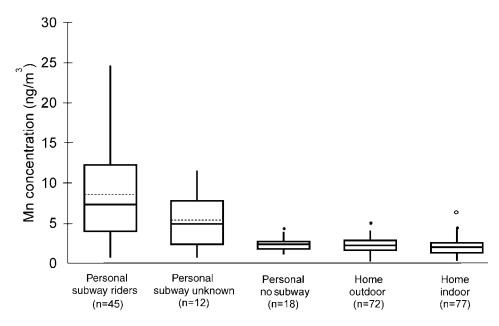


FIGURE 4. Distribution of airborne manganese (Mn) in subsets of personal samples, home outdoor samples, and home indoor samples collected in winter and summer field seasons, where personal samples were broken into three subsets dependent on self-reported commuting activities during air monitoring. The number of measurements in each category is given in the *x*-axis labels. The solid line represents the median, the dashed line represents the average (when different from median), and the box top and bottom represent the 75th and 25th percentile concentrations, respectively. The tips and tails of the whiskers represent the most extreme data point within an inner fence (not marked on diagram) located at 1.5× the interquartile range. Filled circular symbols show moderate outliers or data points that are located between the inner fence and an outer fence defined as 3× interquartile range. Open circular symbols show extreme outliers defined as data points beyond the outer fence.

Pilot Worker Study

Two aims of this study were to explore the range of personal exposures to Mn, Fe, and Cr in the subway environment, and to determine whether there is an association between these exposures and the concentration of these metals and their metabolites in the blood and urine of exposed individuals. Forty transit workers with job duties that are anticipated to have high, medium, low, and little to no exposure to steel dust in the subway system are being recruited to participate in the study. The airborne exposure of each subject is measured by using a personal airsampling device that is carried during work hours throughout one to three work day(s). Currently, we have recruited and monitored roughly half of the study population and predict completing the fieldwork phase of the study by February 2005. At the end of the study period, concentrations of biomarkers of Mn, Fe, and Cr exposure will be measured in blood and urine to compare with the metal concentrations in the personal air samples.

Methods and Analyses Personal air sampling, stationary air sampling, and questionnaires are being used to characterize steel dust exposure levels associated with different job titles, activities, and locations. The personal sampling involves the use

of a portable, battery-operated pump housed in a customized under-the-arm harness. Stationary samplers (filters and particle counters) are placed at selected locations in the subway system for comparison with the steel dust levels measured by personal samplers and to stationary NYC samplers located above ground. Exposure levels and elemental ratios in both personal and stationary samples will be compared. After personal monitoring is completed, each participant is requested to fill out a questionnaire on work environment and activities during a "typical" workday; additional questions address job history, commuting habits, diet, lifestyle characteristics such as engaging in smoking, alcohol, and caffeine, and use of over-the-counter and prescription medications which could affect analyses. Participants are also asked questions to briefly describe their activities during each of the days monitored to determine how that day's work activities (and thus exposure levels) compare with a "typical" workday.

At the end of the personal air sampling, participants are requested to provide samples of urine and blood. Samples are collected in trace metal clean vials and transferred in coolers to the laboratory where they are processed for storage at -20 °C until analyses on all 40 subjects can be performed together. We will measure urine and whole-blood concentrations of Mn and Cr. We understand that blood Mn may not serve well as a biomarker for Mn body burden, but it could serve as an indicator of recent exposure. We are not aware of any prior study that has quantified the absolute amount of Mn absorbed after airborne exposure in either humans or animals.³² Biological samples will also be tested for lead, biomarkers of oxidative stress, and evidence of chromium-induced DNA damage. No enrichment of lead in the subway environment was found in our limited prior sampling. However, as workers have expressed concern about lead exposure, we have decided to include it among our analyses. Oxidative stress may result from the redox potential of transition metals such as Fe, Mn, and Cr. Biomarkers of oxidative stress that may be targeted include 8-oxo-dG (white blood cells and urine) and an assay for oxidized protein (plasma). We will also analyze blood samples for evidence of chromium-induced DNA damage based on tests for DNA-protein cross linking. Because blood Fe levels are strongly regulated, we do not plan on measuring Fe concentrations. However, we will explore the use of Fe isotopes measured in blood samples as a potential indicator of the source of Fe in the blood.³³ Cotinine levels in the blood will also be measured to control for possible exposures to metals in environmental tobacco smoke. Creatinine will be measured in urine to control for degree of hydration. Synchrotron analysis may be used to determine the oxidation states of Fe, Mn, and Cr in airborne particulate matter samples.

Eligibility and Expected Results To minimize intersubject variability of Fe, Mn, and Cr biomarker concentrations due to factors other than recent airborne exposure to steel dust, we developed the following inclusion/exclusion criteria: (1) subjects must not have smoked during the past 6 months; (2) subjects must have worked continuously for the past two years with no continuous absence greater than one month within the last 6 months; (3) subjects must have maintained the same job title (duties) for the past year and must not routinely wear respirators; and (4) subjects must be male. If the study demonstrates a measurable association between personal airborne exposure to steel dust and the levels of different biomarkers of Fe, Mn, and Cr in the biological samples, we plan to investigate these relationships further.

DISCUSSION

Concentrations of steel dust metals observed in NYC subway air and other metro systems around the world fall between outdoor air levels and current Occupational Safety and Health Administration guideline values, above which toxic health consequences may be expected. For example, air concentrations observed for Fe, Mn, and Cr in the single set of duplicate PM_{2.5} samples from the NYC subway are more than two orders of magnitude above ambient NYC levels but three orders of magnitude lower than the Occupational Safety and Health Administration's permissible exposure limit guideline concentrations. As far as we are aware, health effects have not been investigated at these intermediate levels and are thus unknown. The health effects discussed in the introduction are based on epidemiological or mechanistic laboratory studies of Fe, Mn, and Cr at levels that far exceed those currently measured in the subway environment.

Our pilot project of NYC transit workers does not explicitly address health issues of these metals. Rather, it is designed to better define exposure pathways of Mn, Fe, and Cr in the subway environment and to determine whether there is any significant correlation between exposure levels based on personal air samples and changes of potential biomarkers in blood and urine.

CONCLUSIONS

On the basis of job duties and limited sampling to date, subway transit workers are expected to have appreciably higher exposure to steel dust than the commuting public who were previously monitored and shown to have enhanced exposure to Fe, Mn, and Cr that originate from steel dust in the subway system. We are currently recruiting and monitoring forty subway workers with the goals of better understanding the exposures of the workers to steel dust and investigating potential biomarkers of exposure.

ACKNOWLEDGEMENT

Funds for this research were provided by the Mickey Leland National Urban Air Toxics Center (NUATRC-96–01B) and the NIEHS Center for Environmental Health in Northern Manhattan (P30 ES09089). We thank the high school's staff and members of Local 100 of the Transit Workers Union. This is LDEO contribution no. 6718.

REFERENCES

- 1. Chillrud SN, Epstein D, Ross J, et al. Elevated airborne exposures to manganese, chromium and iron of teenagers from steel dust and New York City's subway system. *Environ Sci Technol*. 2004;38:732–738.
- Dwyer J. Subway Lives—24 Hours in the Life of the New York City Subway. New York, NY: Crown Publishers; 1991.
- Shi X, Mao Y, Knapton AD, et al. Reaction of Cr(VI) with ascorbate and hydrogen peroxide generates hydroxyl radicals and causes DNA damage: role of Cr(IV)-mediated Fenton-like reaction. *Carcinogenesis*. 1994;15:2475–2478.
- 4. Klein CB. Carcinogenicity and genotoxicity of chromium. In: Chang LW, ed. *Toxicology of Metals*. New York, NY: CRC Press. 1996:205–219.
- Gorell JM, Johnson CC, Rybicki BA, et al. Occupational exposure to manganese, copper, lead, iron, mercury and zinc and the risk of Parkinson's disease. *Neurotoxicology*. 1999;20:239–247.

- 6. Gwiazda RH, Lee D, Sheridan J, Smith DR. Low cumulative manganese exposure affects striatal GABA but not dopamine. *Neurotoxicology*. 2002;95:1–8.
- 7. Kadiiska MB, Mason RP, Dreher KL, Costa DL, Ghio AJ. In vivo evidence of free radical formation in the rat lung after exposure to an emission source air pollution particle. *Chem Res Toxicol.* 1997;10:1104–1108.
- 8. Costa DL, Dreher KL. Bioavailable transition metals in particulate matter mediate cardiopulmonary injury in healthy and compromised animal models. *Environ Health Perspect*. 1997;105:1053–1060.
- 9. Sitzmann B, Kendall M, Watt J, Williams I. Characterization of airborne particles in London by computer controlled scanning electron microscopy. *Sci Total Environ*. 1999;241:63–73.
- Adams HS, Nieuwenhuijsen MJ, Colvile RN et al. Fine particle (PM2.5) personal exposure levels in transport microenvironments, London, UK. Sci Total Environ. 2001;279:29–44.
- 11. Adams HS, Nieuwenhuijsen MJ, Colvile RN. Determinants of fine particle (PM2.5) personal exposure levels in transport microenvironments, London, UK. *Atmos Environ*. 2001;35:4557–4566.
- 12. Johansson CJ, Johansson P-A. Particulate matter in the underground in Stockholm. *Atmos Environ*. 2003;37:3–9.
- 13. Birenzvige A, Eversole J, Seaver M, Francesconi S, Valdes E, Kulaga H. Aerosol characteristics in a subway environment. *Aerosol Sci Technol*. 2003;37:210–220.
- 14. Furuya K, Kudo Y, Okinaga K, et al. Seasonal variation and their characterization of suspended particulate matter in the air of subway stations. *J Trace Microbe Tech*. 2001;19:469–485.
- 15. Crump KS. Manganese exposures in Toronto during use of the gasoline additive, methylcy-clopentadienyl manganese tricarbonyl. *J Expo Anal Environ Epidemiol*. 2000;10:227–239.
- Pfeifer GD, Harrison RM, Lynam DR. Personal exposures to airborne metals in London taxi drivers and office workers in. 1995 and 1996. Sci Total Environ. 1999;235:253–260.
- 17. Gorell JM, Johnson CC, Rybicki BA, et al. Occupational exposures to metals as risk factors for Parkinson's disease. *Neurology*. 1997;48:650–658.
- 18. Palmer KT, Poole J, Ayres JG, Mann J, Burge PS, Coggon D. Exposure to metal fumes and infectious pneumonia. *Am J Epidemiol*. 2003;157:227–233.
- 19. Aschner M, Vrana KE, Zheng W. Manganese uptake and distribution in the central nervous system (CNS). *Neurotoxicology*, 1999;20:173–180.
- 20. Barbeau A. Manganese and extrapyramidal disorders. Neurotoxicology. 1985;5:13–16.
- Loranger S, Zayed J. Environmental and occupational exposure to manganese: a multimedia assessment. Int Arch Occup Environ Health. 1995;67:101–110.
- 22. Mena I, Marin O, Fuenzalida S, Cotzias GC. Chronic manganese poisoning. Clinical picture and manganese turnover. *Neurology*. 1967;17:128–136.
- 23. Langard W, Norseth T. Chromium. In: Friberg L et al., eds. *Handbook on Toxicology of Metals*. Amsterdam: Elsevier; 1986:185–210.
- Costa M, Zhitkovich A, Toniolo P. DNA-protein cross-links in welders: molecular implications. Cancer Res. 1993;53:460–463.
- 25. Caldwell JC, Woodruff TJ, Morello-Frosch R, Axelrad DA. Application of health information to hazardous air pollutants modeled in EPA's Cumulative Exposure Project. *Toxicol Ind Health*. 1998;14:429–454.
- 26. Wu CY, Pratt GC. Analysis of Air Toxics Emission Inventory: inhalation toxicity-based ranking. *J Air Waste Manag Assoc.* 2001;51:1129–1141.
- 27. Edemé JL, Shirali P, Mereau M, et al. Assessment of biological chromium among stainless steel and mild steel workers in relation to welding processes. *Int Arch Occup Environ Health*. 1997;70:237–242.
- 28. World Health Organization. *Air Quality Guidelines for Europe*. 2nd ed. Copenhagen: WHO Regional Publications; 2000. European Series, No. 91.
- 29. Kinney PL, Chillrud SN, Ramstrom S, Ross J, Spengler JD. Exposures to multiple air toxics in New York City. *Environ Health Perspect*. 2002;110:539–546.

30. Turekian KK, Wedepohl KH. Distribution of the elements in the Earth's crust. *Geol Soc Am Bull.* 1961;72:174–192.

- 31. Metals Handbook, Vol 1, Properties and Selection of Metals. Metals Park, OH: American Society of Metals; 1961.
- 32. Agency for Toxic Substances and Disease Registry (ATSDR). *Toxicological Profile for Manganese*. Atlanta, GA: U.S. Department of Health and Human Services, ATSDR, Division of Toxicology; 2000:175–176.
- 33. Walczyk T, von Blanckenburg F. Natural iron isotope variations in human blood. *Science*. 2002;295:2065–2066.